

# Irreversible Deposition of Line Segment Mixtures on a Square Lattice: Monte Carlo Study

Jae Woo Lee<sup>1</sup>

Department of Physics, Inha University, Incheon 402-751, KOREA

Department of Physics, Clarkson University, Potsdam, NY 13699-5820, USA

## Abstract

We have studied kinetics of random sequential adsorption of mixtures on a square lattice using Monte Carlo method. Mixtures of linear short segments and long segments were deposited with the probability  $p$  and  $1 - p$ , respectively. For fixed lengths of each segment in the mixture, the jamming limits decrease when  $p$  increases. The jamming limits of mixtures always are greater than those of the pure short- or long-segment deposition. For fixed  $p$  and fixed length of the short segments, the jamming limits have a maximum when the length of the long segment increases. We conjectured a kinetic equation for the jamming coverage based on the data fitting.

PACS: 05.70.Ln, 68.10.Jy

---

<sup>1</sup>e-mail:jwlee@munhak.inha.ac.kr

Random sequential adsorption(RSA) is a model of irreversible deposition of fixed-shape objects[1-3]. The objects are deposited randomly and irreversibly on a substrate. When a depositing object overlaps a deposited object, the depositing object is removed from the system and another depositing is attempted sequentially. When we allow a formation of a single layer, the substrate does not reach the full coverage at the long time limit. The jamming coverage  $\theta(t)$  is defined by the total number of covered sites divided by the lattice size. The coverage converges to a particular value, jamming limit  $\theta(\infty)$ , in the long time limit. RSA is realized in experimental studies of protein and colloid particle adhesion on surfaces under the conditions of negligibly slow surface relaxation[4-7].

The theoretical studies including rate equations[8-10], series expansion[11], and Monte Carlo method[12-18] were reported for both continuous and discrete models. Exact solutions are also available for one-dimensional models[13, 14,19-21]. In lattice deposition models the jamming coverage is asymptotically exponential

$$\theta(t) = \theta(\infty) - A \exp(-Bt) \quad (1)$$

where  $A$  and  $B$  are parameters which depend on the dimensionality of the substrate and on the shape of the depositing objects. There are several studies of kinetics of mixture depositions[22-28]. Two different kinds of objects are deposited on the substrate with a different adsorption probability of each object. Exact solutions were reported for RSA of mixtures of monomer and linear  $k$ -mers in a one-dimensional lattice[28]. They showed that the addition of pointlike particles modifies in a nonuniversal way the form of the long-time convergence law of the approach to the jamming coverage. RSA of arbitrary mixtures of line segments of two different lengths were solved analytically on the one-dimensional lattice[29-30]. The deposition on a square lattice of a mixture of line segments of length  $k_1$  and  $k_2$  (end-on model), chosen with equal probability, have been studied by Švrakić and Henkel using Monte Carlo method[26]. They found two inequality relations for the jamming limits

$$\theta(k_1, k_2, \infty) \geq \theta(k_1, \infty) \geq \theta(k_2, \infty) \quad \text{for } k_2 \geq k_1 \quad (2)$$

and

$$\theta(k_1, k'_2, \infty) \geq \theta(k_1, k_2, \infty) \quad \text{for } k'_2 \geq k_2 \quad (3)$$

where  $\theta(k_1, k_2, \infty)$  is the jamming limit of the jamming coverage  $\theta(k_1, k_2, t)$  of a mixture and  $\theta(k, \infty)$  is the jamming limit of single  $k$ -mer. They also proposed the time dependence of the jamming coverage

$$\theta(k_1, k_2, t) = \theta(k_1, k_2, \infty) - A(k_1, k_2) \exp(-B(k_1, k_2)t) \quad (4)$$

with  $B(k_1, k_2) \simeq 1.0$  for  $k_1 \neq k_2$ .

In the present work we have studied kinetics of RSA of mixture having a general deposition probability of each segment, that is, the deposition probability  $p$  for short length of linear  $k_1$ -mers and  $1 - p$  for long length of linear  $k_2$ -mers. Monte Carlo simulations have been performed on a square lattice  $L \times L$ . We used lattices of size  $L = 512$ . We randomly select a lattice site and try to deposit a line segment of length  $k_1$  with the probability  $p$  or length  $k_2$  with the probability  $1 - p$ . We always take  $k_1 \leq k_2$ . If a chosen site is occupied by a deposited object, the attempt fails, the time is increased by one unit, and a new site and a new line segment are selected. If a chosen site is empty, then we randomly select a direction of the four possible orientations. If all  $k_1 - 1$  (or  $k_2 - 1$ ) neighbor sites are empty, the selected sites are occupied. If any neighbor site is occupied by previously deposited object in chosen direction, the attempt fails and the time is increased by one unit and we try a new site. This model is standard model of RSA[25]. In end-on model, all possible directions of a selected site are consumed by occupying selected line segments. After a long time, the system is close to the jamming limit. At late-time stage we check all empty sites. If an empty site has at least one possible direction which is available to accumulate a short line segment  $k_1$ -mer, then empty site is marked as an accessible site. If an empty site has no possible direction to occupy  $k_1$ -mer, that site is an inaccessible site. We further try to occupy line segments at accessible sites. If there are no accessible sites, the system is in the jamming limit. We always use periodic boundary conditions. One Monte Carlo time step is defined by the total number of attempts to select a site divided by the total number of lattice sites. The data are averaged over 50 independent runs for each choice of mixtures and each deposition probability.

We present the typical jamming configuration of mixtures ( $k_1 = 4, k_2 = 16$ ) in Fig. 1 (a) and ( $k_1 = 4, k_2 = 32$ ) in Fig. 1 (b) for the short  $k_1$ -mer deposition probability  $p = 0.5$ . The lattice size is  $128 \times 128$  square lattice with periodic boundary conditions. The configurational structure of jamming

limit has a lot of local structures which have parallel short and long line segments. In Fig. 2 we plot  $\ln[\theta(k_1, k_2, \infty) - \theta(k_1, k_2, t)]$  versus time for  $k_1 = 2$  and  $p = 0.1$ . At long time limit the lines are linear and parallel. In such a standard model the jamming coverages follow the exponential behaviour like eq. (4). We have calculated the slopes of the parallel lines for various length of  $(k_1, k_2)$  pairs and  $p$ . We concluded  $B(k_1, k_2, p) = p/2$  from linear slopes. In Fig. 2 we can observe the independence of  $B(k_1, k_2, p)$  on the length of each line segment. All lines are parallel and the slopes depend only on the deposition probability. These results are different from the observation of end-on model  $B(k_1, k_2, p = 1/2) = 1$ [26] and single adsorption model  $B(k) = 2$ [31]. In end-on model we observed  $B(k_1, k_2, p) = 2p$ [32].

In Fig.3 we show the jamming limits versus the short  $k_1$ -mer deposition probability  $p$  for  $(k_1 = 2, k_2)$  mixtures. The jamming limits decrease monotonically when  $p$  increases. The jamming limit approaches to a value of  $\theta(k = 2, \infty) = 0.9068$  at  $p \rightarrow 1$ . At  $p \rightarrow 0$  the jamming limit shows a singularity. For example, the jamming limit drops to a value of pure single segment deposition  $\theta(k_1 = 2, k_2 = 3, \infty) = 0.8467$  at  $p = 0$ . This singularity was already observed in one-dimensional adsorption of mixtures[30]. For fixed length of  $k_1$  and  $k_2$  we observed that the jamming limit satisfied the same inequality relation as eq. (2). The mixture depositions lead to more efficient jamming coverage than depositions of the single line segment. The jamming coverages are controlled by the long segment of mixtures up to cross-over times  $t_\times$ . At  $t > t_\times$ . The local empty spaces are shorter than the length of the long segments. Therefore, the short segments are further adsorbed on the substrate.

In Fig.4 we plot the jamming limit  $\theta(k_1 = 2, k_2, \infty; p)$  versus the length of a long segment for fixed length of short segment  $k_1 = 2$  and various  $p$ -values. For a fixed value  $k_2$ , the jamming limits satisfy  $\theta(k_1, k_2, \infty; p_2) > \theta(k_1, k_2, \infty; p_1)$  when  $p_2 > p_1$ . For a fixed value  $p$  the jamming limits reach a maximum value at a particular value  $k_2^*$ . A combination  $(k_1, k_2^*)$  of mixtures at a fixed value of  $p$  gives the most efficient jamming coverage at long time limit. We check the finite size effects for  $p = 0.5$  using  $256 \times 256$  and  $1024 \times 1024$  lattices. We observed that the effects of finite size are negligible. We concluded that these maximum behaviours are intrinsic in mixture deposition on such a standard model. We also observed the maximum behaviour for end-on model at a certain range of the probability  $p$ . (These results will be published elsewhere[32].) When the length of the long segments increases

for fixed length of  $k_1$ , the adsorbed long segments induce that the newly adsorbing long segments locally have the same direction as adsorbed one as shown in Fig. 1 (b). Among the adsorbed parallel long segments, the short  $k_1$ -mers further adsorbed to the direction of the long  $k_2$ -mers. These adsorptions induced local one-dimensional characteristics of the short segments and the jamming limits decrease for  $k_2 > k_2^*$ .

We have performed the data fitting to check the parameter dependence of the amplitude  $A(k_1, k_2, p)$ . We concluded that the amplitude has the functional form as  $A(k_1, k_2, p) = C_o(1/k_1)^2 \exp[C_1(1 - p) + C_2(1 - p)/k_2]$ . The amplitudes are well fitted for the choice of the constant  $C_o = 0.8 \pm 0.1$ ,  $C_1 = -0.5 \pm 0.2$  and  $C_2 = -1.3 \pm 0.1$  for all  $k_1 \leq k_2$  mixture combinations[32].

In summary we observed that the mixture depositions cover the substrate more efficiently than the deposition of single-length segments. We observed that the jamming limits show a maximum behaviour for fixed  $k_1$  and  $p$  when the lengths of  $k_2$  vary. The jamming coverage shows exponential behaviour. We proposed a functional form of the amplitude of coverage from the data fitting.

*This work has been supported by Inha University and by the Basic Science Institute Program, Ministry of Education, Project No. BSRI-97-2430. I wish to thank Professor Vladimir Privman for his critical reading of this manuscript.*

## References

- [1] J. W. Evans, Rev. Mod. Phys. **65**, 1281(1993).
- [2] M. C. Bartelt and V. Privman, Int. J. Mod. Phys. B **5**, 2883(1991).
- [3] V. Privman, Trends Stat. Phys. **1**, 89(1994).
- [4] P. J. Flory, J. Am. Chem. Soc. **61**, 1518(1939).
- [5] J. Feder and I. Giaever, J. Colloid Interf. Sci. **78**, 144(1980).
- [6] G. Y. Onoda and E. G. Linger, Phys. Rev. A**33**, 715(1986).
- [7] V. Privman, N. Kallay, M. F. Haque and E. Matijević, J. Adhesion Sci. Technol. **4**, 221(1990).
- [8] J. Evans and R. S. Nord, J. Stat. Phys. **38**, 681(1985).
- [9] P. Schaaf, J. Talbot, H. M. Rabeony and H. Reiss, J. Chem. Phys.**92**, 4826(1988).
- [10] P. Schaaf and J. Talbot, Phys. Rev. Lett.**62**, 175(1989).
- [11] R. D. Vigil and R. M. Ziff, J. Chem. Phys.**91**, 2599(1989).
- [12] M. Nakamura, Phys. Rev. A**36**, 2384(1987).
- [13] P. Nielaba, V. Privman and J. S. Wang, J. Phys. A**23**, L1187(1990).
- [14] P. Nielaba, V. Privman and J. S. Wang, Phys. Rev. B**43**, 3366(1991).
- [15] J. D. Sherwood, J. Phys. A**23**, 2827(1990).
- [16] R. M. Ziff and R. D. Vigil, J. Phys. A**23**, 5103(1990).
- [17] M. C. Bartelt and V. Privman, J. Chem. Phys.**93**, 6820(1990).
- [18] B. Bonnier, M. Hontebeyrie, Y. Leroyer, C. Meyers and E. Pommiers, Phys. Rev. E**49**, 305(1994).
- [19] B. Widom, J. Chem. Phys.**44**, 3888(1966).
- [20] R. Pomeau, J. Phys. A**13**, L193(1980).
- [21] R. Swendsen, Phys. Rev. A**24**, 504(1981).
- [22] B. Mellin and E. E. Mola, J. Math. Phys. **26**, 514(1985).
- [23] B. Mellin, J. Math. Phys. **26**, 1769,(1985), **26**, 2930(1985).
- [24] G. C. Barker and M. J. Grimson, Mol. Phys. **63**, 145(1988).
- [25] R. S. Nord and J. W. Evans, J. Chem. Phys.**93**, 8397(1990).
- [26] N. M. Švrakić and M. Henkel, J. Phys. I **1**, 791(1991).
- [27] Lj. Budinski-Petlović and U. Kozmidis-Laburić, Physica A **236**, 211(1997).
- [28] M. C. Bartelt and V. Privman, Phys. Rev. A**44** R2227(1991).
- [29] G. J. Rodgers, Phys. Rev. A**45**, 3443(1992).
- [30] B. Bonnier, Europhy. Lett. **18**, 297(1992).
- [31] S. S. Manna and N. M. Švrakić, J. Phys. A**24**, L671(1991).
- [32] J. W. Lee, *in preparation*

## Figure Captions

Figure 1: Typical configurations of mixture deposition on  $128 \times 128$  square lattices for (a)  $k_1 = 4, k_2 = 16$  and (b)  $k_1 = 4, k_2 = 32$ .

Figure 2: The plot of  $\ln[\theta(k_1, k_2, \infty) - \theta(k_1, k_2, t)]$  versus time for  $k_1 = 2$ ,  $p = 0.1$  and  $k_2 = 4, 8, 16, 32, 64$  from bottom to top.

Figure 3: The jamming limits versus the short segment deposition probability  $p$  for  $k_1 = 2$  and  $k_2 = 3(\diamond)$ ,  $4(+)$ ,  $8(*)$ ,  $16(\triangle)$ ,  $32(\square)$ , and  $64(\times)$ .

Figure 4: The jamming limits  $\theta(k_1 = 2, k_2, \infty; p)$  versus the length of the long segment for a fixed length of the short segment  $k_1 = 2$  and  $p = 0.1(\triangle)$ ,  $0.3(\times)$ ,  $0.5(\square)$ ,  $0.7(+)$ , and  $0.9(\diamond)$ .









